Summary

Nature has intrigued and inspired man for millennia with its beauty and fascinating molecular systems allowing complex functions to be performed. In the past few billion years, self-assembly is a fundamental principle employed by Nature to construct elegant and intricate molecular machinery, which is key to life on the earth. Self-assembly in nature is often based on numerous hydrogen bonding, van der Waals and many other weak inter/intramolecular interactions in a cooperative manner. In recent years, self-assembly has been employed to create complex artificial molecular machines and smart materials. One of the major challenges is to build responsive systems of which the function can be regulated by external stimuli. Various studies have been focused on the fabrication of smart functional materials where physical properties and functions emerging from large molecular self-assemblies can be controlled at will. Photoresponsive self-assembled systems are particular attractive. Distinctive approaches are shown in Figure 1.

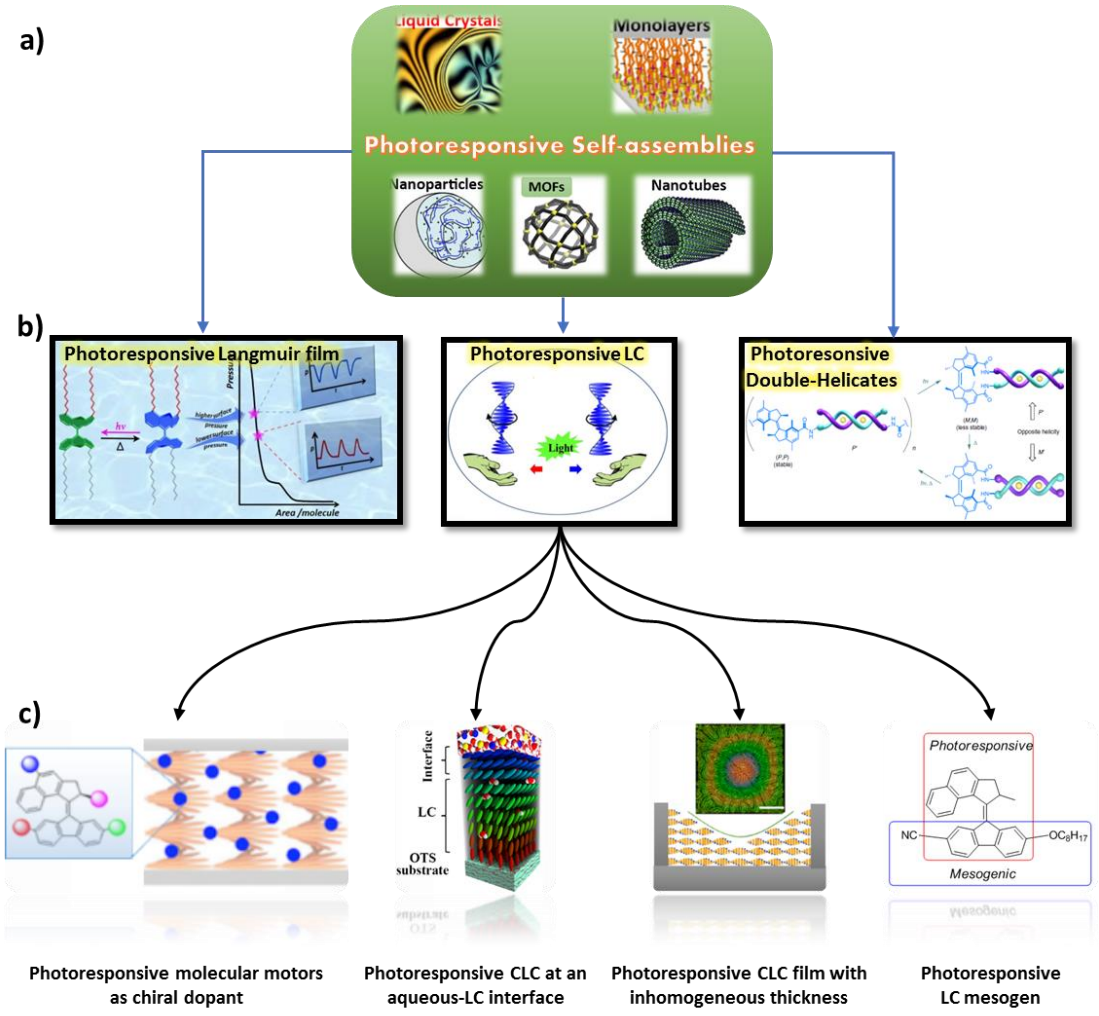

Figure 1. a) Strategies for constructing photoresponsive self-assemblies and their applications, b) Strategies described in this thesis and c) Photoresponsive LC studies reported here.

The aim of this thesis is to develop smart materials based on photoresponsive self-assembled systems, with a special focus on Langmuir film, liquid crystals (LC), and helicates (Figure 1b). In this thesis, as shown in Figure 1, we have utilized a variety of responsive molecules based on light-driven molecular switches or motors in these three classes of materials and studied their responsive behavior.

Chapter 1 gives a literature review on self-assembly processes and self-assembled systems which can be controlled by external stimuli. The first part of the chapter highlights different kinds of self-assemblies, describing several strategies to construct self-assemblies based on noncovalent interactions. In the second part, a brief overview on different classes of photochromic compounds (molecular switches and motors) and their switching mechanisms is presented. In the third part, the incorporation of photochromic molecules into self-assembled systems is illustrated with recent literature examples.

In **Chapter 2,** a photoresponsive Langmuir film based on amphiphilic overcrowded alkenes is presented. The amphiphile is able to self-assemble at the air-water interface to form a stable Langmuir monolayer by itself or by mixing with Dipalmitoylphosphatidylcholine (DPPC). It was observed that the efficient photoisomerization of the *anti*-folded to *syn*-folded geometry of the amphiphile's central core induced changes in the surface pressure in either direction, depending on the initial packing. Additionally, the switching behavior can be regulated in the presence of DPPC, which influences the packing of the molecules, thereby controlling the transformation of the LB film upon irradiation.

Chapter 3 focuses on the development of a family of second-generated molecular motors with different substituents at various positions and their application as chiral dopants in LCs. It was found that the geometrical changes alter the intermolecular compatibility between the chiral dopants and the LC materials. As a result, the sign and helicity of the superstructure of LC matrix can be modulated through the photochemical and thermal isomerization of molecular motors. The geometrical changes, which are associated with the changes of chirality of the motors, are able to induce the reorganization of the LC superstructures. This responsive behavior was further demonstrated by controlling the macroscopic rotational motion of micro-size objects on the top of LC films.

In **Chapter 4**, the interfacial interaction between an aqueous layer and cholesteric LC film was investigated. The helical pitch of the cholesteric LC and the concentrations of surfactant (SDS) in the aqueous phase are two key elements to control the aqueous-LC phase interaction. The helical pitch can be modulated by doping molecular motors with different concentrations, while the photochemical and thermal isomerization of molecular motors is found to regulate the aqueous-LC interaction as well.

In **Chapter 5**, photoresponsive cholesteric LCs were confined in copper TEM grids, by which a LC film with inhomogeneous thickness could be obtained. Notably, the topological structures can be remotely controlled by UV irradiation, which are highly dependent on the thickness

of the LC films. It has been found that at the center of the curved CLCs where the LC film has minimum thickness, photoisomerization of the motor is more effective than that at the edge of LC film, which consequently induced the unwinding and subsequently rewinding process of CLCs in a directed manner (from inside to outside).

Chapter 6 described, to the best of our knowledge, the first examples in which an unidirectional rotary motor connecting oligobipyridyl ligands, which can dynamically change their chirality upon irradiation, assemble into metal helicates that are responsive to light. It was shown that the self-assembly process as well as the helical chirality, the switching between oligomers and double-stranded helicates with different handedness can be controlled by the rotary motor scaffold. If the motor unit adopts a *trans*-geometry, the two ligand strands will be remote from each other and an oligomeric array was expected. Isomerization to the *cis* form will bring the two ligand strands in close proximity, allowing the formation of a double helicate upon copper binding, while the chirality (helical sense) is controlled by the configuration of the *cis* motor unit. The inversion of the chirality of the helicates, from metastable to stable helicates, is driven by the strong tendency of the motor to invert helicity when the isomerization from less stable (*M,M*)-*cis*-isomers to stable (*P,P*)-*cis*-isomers occurs.

Chapter 7 focused on the development of a new photoresponsive LC mesogen. Second-generation molecular motors (*trans*/*cis* M3) containing intrinsic 4,4'-disubstituted biphenyl were designed and synthesized. The correlation between the molecular structure, electronic factors and photoresponsive properties is discussed. Although *trans/cis* **M3** does not display intrinsic LCs properties, which might be due to the steric hindrance, the distinct isomers are still effective as chiral dopants in nematic LC materials.

Overall, the experimental works presented in this thesis contributes to the development of various self-assembled systems and how these systems are controlled in a dynamic fashion. The switching of the self-assembled materials can *e.g.* be used to control the surface tension of the monolayer, the helicity of the liquid crystalline, the orientation of LC molecules at the aqueous-LC interface and the chirality of metal helicates. The insight and knowledge gained by studying these fascinating self-assembled systems may bring new opportunities for potential applications, including biosensors, light-driven molecular machines, photo-displays, and responsive surfaces, etc. While self-assembly has inspired us to construct and explore intricate molecular machinery, its full potential has yet to be uncovered and I hope the work presented in this thesis stimulates many future discoveries in the field of responsive supramolecular materials.